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**FLOW INJECTION PRECONCENTRATION
COMBINED WITH DIRECT SAMPLE INSERTION
FOR INDUCTIVELY COUPLED PLASMA SPECTROMETRY**

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INTRODUCTION

The Inductively Coupled Plasma (ICP) has established an enviable performance record as a source for both atomic emission spectrometry (AES) and mass spectrometry (MS). While matrix effects in ICP-AES are only moderate, it lacks the sub part-per-billion (ppb) detection limits of ICP/MS. On the other hand, ICP/MS suffers from a wide variety of matrix effects [1] which can affect the accuracy of the system. In our laboratory we have experimented with Direct Sample Insertion (DSI) [2] for liquid sample analysis by ICP-AES and ICP/MS. While detection limit advantages are gained with DSI in both AES and MS, DSI-ICP/MS offers the additional advantage of a significant reduction in matrix effects by eliminating the solvent from the sample introduction process [2].

Flow Injection (FI) has been used extensively in configurations commonly called Flow Injection Analysis (FIA) systems [3], and more recently as an approach to extending the capabilities of atomic spectrometry [4]. FI preconcentration offers two important benefits for ICP spectrometry. The first is the preconcentration advantage, generally between one and two orders of magnitude [5-8]. The second advantage arises from the separation of the analytes from interfering matrix constituents. Samples which have undergone the FI preconcentration

treatment emerge from the system in the same matrix, namely, that of the eluant. This has advantages for ICP spectrometry, particularly ICP/MS, which is more sensitive to matrix effects than ICP-AES.

One loses a great deal of the advantage of preconcentrating the sample if a significant fraction does not reach the plasma. The low transport efficiency (between 1-5%) of most nebulizer/spray chamber combinations indicates that a special advantage for FI-ICP spectrometry may be gained by using DSI, which provides a sample introduction efficiency of 100%. While previous liquid DSI-ICP-AES and DSI-ICP/MS work in our laboratory was oriented towards the use of wire loops [2,9], there have been several recent reports in the literature that either a thin-walled thin-stemmed graphite cup or a deep undercut electrode give excellent performance with liquid samples [10,11]. These configurations reduce cup mass and facilitate rapid heat transfer to the sample, resulting in narrower, more intense peaks. In our previous report [12] we discussed both the development of special graphite probes for FI-DSI-ICP-AES and the experimental aspects of the method.

In this paper we have addressed the question of the expected "multiplicative effect". It would seem that the preconcentration factor of the FI front end could be almost directly multiplied by the detection limit improvement of DSI-ICP. Since both advantages are significant, about a factor of 10, the combination of the two should provide a stunning improvement, of about two orders of magnitude.

RESULTS AND DISCUSSION

The operating parameters for the flow injection system and the DSI system were optimized separately, as there was no reason to expect any interaction between the two subsystems. The Chelex-100 ion exchange resin columns were optimized with respect to length and inner diameter. "Optimal" in this case was determined to be the column that gave the highest intensity signal in the smallest time window for a fixed sample volume without exceeding the loading capacity of the column. The other operating parameters that were varied include sample loading rate, pH of the buffer, acid strength and elution flow rate. These experiments were normally conducted by running the eluant directly into a nebulizer/spray chamber system.

The precision of determinations at the 5 ppb level (about 100 times the detection limit with clean blanks) using peak integration for the three elements averaged 4% RSD using manual drying of the eluant into a cup. Although this precision is quite good, there is potential for improvement since the DSI system has previously exhibited precisions for liquid work of about 1% [9] when automated.

By collecting small fractions of eluant, it was determined that a 5.0 mL injection volume eluted in approximately 160 μ L providing a preconcentration factor of 30, typical of many of the systems described above. Detection limit improvements ranging from $\times 10$ to $\times 100$ (element specific) have been reported [8] for DSI alone. In Table 1 we have presented detection limits for DSI obtained independently of the FI system. One would then expect that the product of the DSI Improvement Factor and FI Preconcentration Factor would produce detection limit improvements of the magnitudes shown in Table 1. The performance data obtained are given in Table 2. The thin walled cup detection limits of Table 1 were obtained with a slightly different optical arrangement (viewing height and lens position) than that used for the final set of

experiments which provided the data in Table 2. Nevertheless, the observed multiplicative effect is certainly of the same order as that predicted.

Table 1. FI-DSI-ICP-AES Performance Expectations

Element	Nebulizer Detection Limit (ppb)	DSI Thin Cup Detection Limit (ppb)	DSI Improvement Factor	FI Preconcn. Factor	Expected Improvement Factor
Pb	30	0.9	30	30	900
Zn	80	0.6	130	30	3900
Cu	8	0.9	9	30	270

Table 2. FI-DSI-ICP-AES Performance Data

Element	Nebulizer Detection Limit (ppb)	Ideal Blank Detection Limit (ppb)	Improvement Factor	Real Blank Detection Limit (ppb)	Improvement Factor
Pb	30	0.05	600	0.04	700
Zn	80	0.07	1200	1	80
Cu	8	0.06	140	0.2	40

As the relatively high nebulizer detection limits in Table 2 reveal, the spectrometer could be considered somewhat sub optimal. Several nebulizers (Meinhard and Légère) imported from a conventional spectrometer provided the solution detection limits presented when used with this system, yet these nebulizers performed up to factory specifications on a newer system, usually providing detection limits about an order magnitude better. Since the purpose of the experiments was to establish the general validity of the multiplicative effect, we are extremely pleased with our results. It is however unfortunate that the optics had not been brought up to optimal at the time of these experiments. None-the-less, detection limits in the 50 ppt range are encouraging at this stage.

Since we do not have an in-house ICP/MS system, this was our first experience working at sub ppb levels. Our first experiments with the system demonstrated that the blank levels were very high. After several changes of reagents and the installation of guard columns, the blanks were reduced drastically, but continued to be quite high, with signals corresponding to 0.2, 3 and 0.8 ppb of Pb, Zn and Cu respectively. Some detective work revealed that both the valves on our injection system, which has been in use for two years, were contaminating the system. One column of the data in Table 2, labelled "real", was collected using the less contaminated of the valves. The first set of detection limits, called "ideal", was determined using doubly distilled water in a DSI cup as the ideal blank. The improvement factors were calculated using both sets of data.

We have made no attempt in this study to demonstrate the linearity of calibration curves. Both separations methodologies [13] and DSI technologies [9] have demonstrated a linear response over at least three orders of magnitude. While this would indicate that curves would be linear, it will be critical to evaluate the performance when we move on to more extensive testing. We have also not attempted to further reduce detection limits by increasing the sample volume. Elementary theory indicates that a linear improvement would be expected as long as the column loading capacity was not approached. If implemented under the same operating conditions, the price paid would be a proportional increase in analysis time.

CONCLUSIONS

Considerable effort on our part was expended during the earlier stages of this work to develop a convenient automated FI-DSI interface. Our efforts were primarily directed at depositing the FI eluant on wire loops, which we felt would provide the best detection limits. The difficulty of achieving this interface led us to change to graphite electrodes as probes. The excellent wire loop detection limits were, in large part, due to the rapid heating of the loop. This observation encouraged us to develop an extremely thin walled, narrow stem electrode. This does not imply that graphite cups are necessarily the ultimate solution. Our expectation is that a system which sprays the eluant onto a hot surface would provide a suitable interface. The surface could be either a DSI probe or an electrothermal vaporization (ETV) system. The ETV configuration offers a number of potential advantages which are worth mentioning.

1. Convenient control of the drying step since the capability is integral in the design.
2. Rapid switching between conventional liquid introduction and ETV introduction.
3. More control of the experiment by decoupling the vaporization and excitation systems.

It is important to note that some elements generally do not provide the excellent performance of the elements selected for this test, due to the formation of non-volatile carbides. This is not to say that these elements can not be determined by this approach; there appear to be at least two ways to address the problem. The first is to use metallic DSI probes [9,11] or ETV boats. There would then be some concern that the acidic solutions used with an ion exchange preconcentration column would corrode the probe and introduce significant contamination. There are several FI preconcentration modes [8,14] which elute the analyte in a

complexed form after either an ion exchange or an adsorption column. The eluants are considerably less corrosive than the strong nitric acid that is used for traditional ion exchange. Alternatively, if the complex can survive the drying process on a graphite surface, it may provide a volatile carrier for the bound metals, thereby furnishing even better performance (sharper peaks) while reducing concerns about carbide formation.

We are pleased to observe the multiplicative effect that one would expect with a complementary hybrid arrangement of this type. FI-DSI-ICP spectrometry seems to offer the potential for bringing ICP/MS detection limits to ICP-AES, as well as providing the other advantages of FI sample handling. While not demonstrated in this work, a natural by-product of the separation phenomenon would be a reduction of ICP/MS matrix effects, perhaps to levels matching or less significant than those of ICP-AES. One would also expect detection limit benefits for FI-DSI-ICP/MS to accrue.

DSI systems have demonstrated relative standard deviations of less than 1%. Similar performance is possible with FIA systems. Our precision of 4% leads us to believe that there are significant advantages to be gained in detection limits, reproducibility, and general operating performance, by developing an automated interface between the FI and the DSI systems. In fact, an automated interface would seem to us to be one of the most important obstacles to overcome before this technique can achieve a wide level of acceptance.

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